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- COMMUNIST CHINA -

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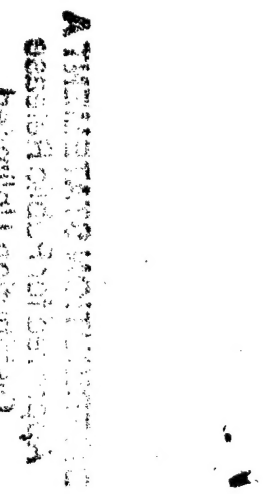

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A NEW METHOD OF ZONE MELTING FOR REFINING SUPER-PURITY GALLIUM

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/Following is a translation of an article by Liu Min-chih, Institute of Physics, Academia Sinica, in Wu-li Hsueh-pao, Volume 15, Number 7, July 1959, pp. 389-392./

ABSTRACT

This paper describes a new method for refining super-purity Ga (99.9999%). This method provides multiple zones on one side of the helix of plastic tubing in which the material to be refined is filled. Thus, when the helix rotates, the melting zones travel endlessly throughout the specimen. The efficiency of this arrangement is thought to be higher than that of the conventional one.

Utilizing the fact that impurities tend to concentrate more in the liquid phase than in the solid phase of a material, R. S. Jessup in 1940 suggested that this property can be used to purify matter. He proceeded to use this method to purify benzoic acid. In 1944, F. W. Schwab and E. Wickers used this method to purify benzoic acid and acetanilide. In 1952, W. G. Pfann used this method to obtain super-purity metal. This method is now called the zone melting method. Many metals can now be purified with this method. In certain elements, such as Germanium, the impurity can be reduced to 10^{-10}.

As to the techniques of this zone melting method, many different ways have been used. So far as we know, there are: the commonly used straight line zone melting method, the ring shaped zone melting, the floating zone melting, the bird cage type zone melting, the electron

bombarding floating zone melting, the magnetic floating zone melting, etc. These different methods are used according to the different properties of the matter to be purified.

For the purification of Gallium, D. P. Detwiler and W. M. Fox used the straight line zone melting method. They filled a straight glass tube with Ga and used resistance coil heating to create the melting zones. In between the melting zones, cold water was circulated to create the solidifying zones. J. L. Richards added nitric acid to the impure Ga to create $GaCl_3$. He then used the zone melting method to refine the Gallium tri-chloride, finally reducing it to high purity Gallium by hydrogen reduction. The first method mentioned needs complicated apparatus and the purification efficiency is not high. The loss due to Ga's adhesion to the glass tube is also quite large. The second method involves several steps, which are both care-taking and time-consuming.

In the case of the straight line zone melting method, one can save time by setting up several melting zones and move them back and forth within each section simultaneously. (Suppose the metal specimen has length L, and the number of melting zones is n. Then each melting zone will have to move a distance of D= L/n before getting back to its original position for the next round.) In principle, this method is n times faster than the single zone melting method. However, due to the non-uniform movement between the heater and the melting zone, some undesired solidification will occur between the neighboring parts of the melting zones. Consequently, the impurity concentration there will be more than in the other parts. This is even more pronounced at the end of the specimen, where the impurities gather. In other words, if one just compares the efficiency per passing, this multiple zone refining method is not as good as the single zone method.

If one makes the specimen into the ring shape, than the melting zones can move circularly around. This ellminates the back and forth motion which is the drawback for the straight line samples. Hence, the afore mentioned shortcomings can be avoided. However, the difficulty here is that a ring shaped mold is much harder to make. Moreover, one has to break the mold each time. In addition, a ring shaped heating system is also difficult to make. These explain why this method sees only limited use.

Here we suggest to use a helix zone melting method for purifying Gallium. The principle of this method is to apply the straight line zone melting method to a helix metal specimen. The apparatus is shown in Fig. 1.

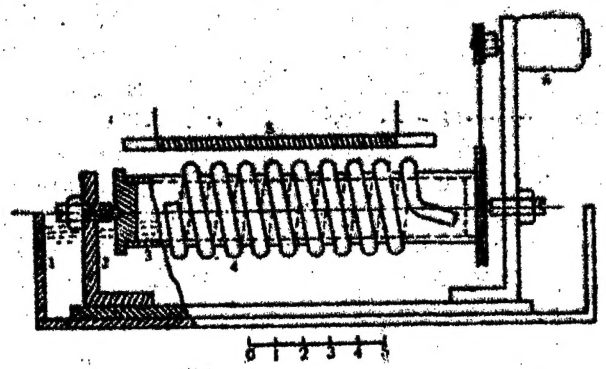

Fig. 1
A diagram of a helix zone melting apparatus
1. Cooling water trough. 2. Supporting arm.
3. Glass tube. 4. Plastic tubing filled with Ga. 5. Resistance heater coils. 6. Synchronized electric motor.

As can be seen, this setup allows multiple zone melting. For each rotation of the helix, a new zone comes in and an old one goes out. It does not have the discontinuous region which is the chief drawback of the straight line zone melting method. The result is then exactly n times the efficiency of a single zone refining. It is worth noting that we have also elliminated the time needed to bring the heater back alltogether.

Gallium has a low melting point of 29.8 c and a high boiling point of 1983°c. The sample we used is made in China and it contains Zn, Pb, Cu, Fe. At 1000°c their vapor pressures are: Ga - 8×10^{-3}, Zn - 4×10^{4}, Pb - 1.8, Cu - 5×10^{-4}, Fe - 8×10^{-5}, all in mmHg. To elliminate Zn and Pb and other volatile impurities, we first fill the Ga sample half full in a transparent quartz tube about 15 cm long and 2.5 cm in diameter. It is then distilled for about 4-6 hours at 1000°c in a vacuum of 10^{-2}mmHg as shown in Fig. 2.

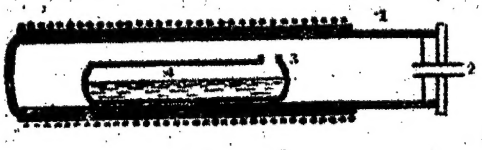

Fig. 2
High temperature vacuum treatment of Ga.
1. High temperature furnace. 3. Quartz boat.
2. Vacuum pumping connections. 4. Gallium specimen.

After that treatment and cooling to about 30 to 40°c, the Gallium specimen is poured into clear plastic tubing, 4 - 8 mm in diameter, with the help of a small funnel, plastic or quartz, to avoid the strong adhesion between glass and Ga. The ends of the plastic tubing are tied up with cotton thread. Air bubbles inside are to be avoided. Before the Ga solidifies, the plastic tubing is wound onto the rotatable glass cylinder (3 cm diameter) as shown in No. 3 of Fig. 1. Several small holes (5 mm diameter) have to be drilled on the glass cylinder wall so that cold water can flow inside to keep the temperature uniform. The spacing between the turns of the helix is kept at 3 to 5 mm. It can not be too small or the water will come up along the narrow edge and cause incomplete melting near the wall.

The use of plastic tubing has several advantages. It will not break by the expanding Ga during solidification. It will not be contaminated by metals inside and it can easily be wound onto the desired helix.

The rotatable glass cylinder is supported on two ends and is rotated by a small synchronized electric motor. It can be taken down to facilitate the replacement of the plastic tubing when the refining is done.

A bar shaped resistance heater is placed horizontally along the cylinder. The distance between them can be adjusted. The metal or glass cover above it acts as a reflector to concentrate the heat radiation. It also stops irregular air current and thus regulates the temperature. The size of the melting zones must be uniform and stable if high efficiency is to be obtained. A self-adjusting transformer can be used to regulate the temperature of the melting zones at about 50 - 60°c. The melting zone should not go over the top part of the helix.

Due to the fact that Ga has a long temperature range of super cooling, sometimes to as low as -40°c, the helix must not only be half-bathed in a tank with circulating water, but a solid crystal must also be kept before the first melting zone so that the melted Ga may solidify at the water temperature. Otherwise, a much lower temperature is needed to create the solidifying condition. In our case, the crystal is kept in a small portion of the plastic tubing just outside of the heater range so that it will remain solid throughout the refining process.

Gallium contracts in liquid phase, thus it tends to move gradually toward the ends of the plastic tubing after several zone melting operations. To avoid the danger of breaking the tubing, the following two methods may be used. The first is to loosen the real end or plug it with

a plastic stop and leave an empty space for the expanding Ga. Another method is to place all melting zones, i.e., the heating coil, on the side of the helix where it turns into the water. This is analogous to the usual practice of tilting forward a degree or two in a straight line zone melting to keep the cross section uniform. Of these two, we found the second method to be better.

The apparatus we used has the following specifications: the rotating glass cylinder's diameter is 3 cm, the length 30 cm; the plastic tubing's outside diameter is 5.6 mm and the inside diameter is 4.8 mm, with a length of 150 cm; the mean circumference of the Gallium helix is 11.8 cm. The electric motor for rotating the glass cylinder is the same kind used on the common electric clock. It rotates the cylinder once every three hours and with an equivalent linear velocity of 3.9 cm/hour. It rotates the cylinder eight turns per day and stops after 40 turns. With this arrangement, one obtains 150 grams of super purity Ga for every load of 180 grams Ga specimen. If the plastic tubing has an outside diameter of 7.2 mm, an inside diameter of 6.4 mm and a length of 150 cm, then it can hold 300 grams of Gallium and yield 250 grams of super purity Ga each time.

Because the distribution constants for Pb, Cu, and Fe have $K>1$ and for Zn, $K<1$, we must cut off both ends of the helix. The front end, which enters the water first, contains Pb, Cu, and Fe impurities and two rings are cut off from it. The other end contains Zn impurities and one ring is cut off there.

From our preliminary experiment, the refining result is as follows:

	Zn %	Pb %	Cu %	Fe %	Ni %
Original specimen 99.9%	0.03	0.04	0.01	0.005	0.000
After Treatment	—	—	<0.0001	<0.00001	0.0000
Original Specimen 99.9882%	0.0018	0.01	0.0008	0.0002	0.000
After Treatment	—	—	<0.0001	<0.00001	0.0000

From the above chart, one sees that the refined Ga can attain a purity to 99.9999%.

For large scale industrial production of super purity Ga, one can place Ga in a transparent quartz tube or a specially treated high purity graphite trough. The whole thing is then placed in an aluminum oxide tube under 10^{-2} mm Hg vacuum for 4 to 6 hours at 1000°c to rid itself

of Pb and Zn. Then it may be treated with the zone melting method as described above. The plastic tubing and glass cylinder can be enlarged appropriately. One motor can be used to rotate several cylinders. One heater may be placed between two parallel glass cylinders to heat both, etc.

To sum up, the helix zone melting method has the following six advantages.

1. Simplicity in operation, unlike the commonly used methods of D. P. Detwiler and W. M. Fox, or J. L. Richards.
2. It greatly shortens the time needed for purification. Our sample has a total length of 150 cm. With the same speed, a single zone straight line zone melting method requires 42 hours, while our method requires only three hours, because we have 14 melting zones in all.
3. It is superior to the usual back and forth multiple zone method in that it does not have connecting regions and so has more uniform distribution.
4. The use of plastic tubing reduces the loss due to adhesion and contamination.
5. It is suitable both for laboratory experimentation and for large scale industrial production.
6. The refining apparatus is inexpensive.

In the future, if the operating temperature of plastic tubings can be raised to 500°c, then many low melting point metals (In, Se, Sn, Bi, Tl, Cd, Pb, Zn, Te) can all be super-purified by this method.

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